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(54) Method of producing painted metal sheets

Verfahren zur Herstellung von lackierten Metallblechen

Méthode pour la production de tôles métalliques peintes

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Description

[0001] The present invention is related to a method for producing a pre-painted metal substrate, in terms of a sheet, comprising a painting step and a curing step. In particular, the present invention is related to the production of pre-painted weldable metal sheets.

State of the art

[0002] In the automobile industry, there is a great need for metal coated steel sheets. The metal coating may consist of a zinc-containing layer, for example applied by electro galvanising or hot dip galvanising. In recent years, the use of pre-painted steel sheets has become important. To produce these pre-painted sheets, an organic weldable paint layer is applied on top of the metal coating.

[0003] The curing of these paint layers is determining the eventual quality of the pre-painted sheet. Classically, curing is done by convection. This method however causes problems of flexibility, in terms of longer production times and costs.

[0004] One of the important elements of weldable organic painted sheet is the design of the mechanical and/or chemical bond between the metal sheet and the organic paint layer. A pre-treatment is always performed on the metal sheet, in order to acquire a layer with a suitable composition onto which the paint will be applied. A crucial factor in the quality of the paint layer is the interface between this pre-treatment layer and the eventual paint layer. On the one hand the interface should be strong enough to ensure good adhesion and good corrosion protection, in particular protection against hem flange corrosion. On the other hand the interface should be sufficiently conductive to allow very good welding, above all spot welding. Heavy metal rich pre-treatment layers such as layers containing chromates are well known in the art.

[0005] However, environmental regulations are causing these heavy metal rich pre-treatment layers to be stepped down in favour of heavy metal free pre-treatment layers, for instance very thin organic layers containing metal complexes, very thin layers of metal oxides or layers of functional molecules. These heavy metal free pre-treatments suffer however from lower performance in terms of adhesion and corrosion, which is due to the insufficiency of existing curing methods.

[0006] The curing of the pre-painted sheets takes place immediately after the painting step, when a liquid paint layer is present on the sheet. During the curing process, three phenomena should take place:

- removal of solvent from the paint layer by evaporation of said solvent;
- film forming of the paint layer: as the solvent is removed, the paint forms a layer with a higher viscosity than the liquid paint, but which is soft enough to fill up the pores of the pre-treatment layer and thus form a mechanical connection between the organic paint layer and the metal;
- polymerisation: forming of chemical connections inside the paint layer and between the paint layer and the pre-treatment layer.

[0007] The two last steps are crucial to form a high quality bond within the interface pre-treatment layer/paint layer, and are further described as the 'activation' of said interface.

[0008] Curing methods work by applying heat to the wet paint layer. However, existing methods do not allow an optimal realisation of the above mentioned steps. This is because they cause these steps to take place gradually, from the top of the layer, to the bottom: this causes the top of the paint layer to start forming a soft film, before all of the solvent underneath has been able to evaporate. As a consequence, pockets of solvent become trapped in the paint layer, leading to voids inside the layer, or erupt through the top film, thereby forming craters in the surface. The proper activation of the interface between pre-treatment layer and paint layer is hampered by these deficiencies, leading to a decreased paint adhesion. Craters can be so large as to expose the underlying metal, or in any case, they cause an inhomogeneous conductivity of the resulting layer. This will eventually lead to inferior quality of the base coat and top coat which are applied on top of the pre-painted sheets, for example in the automobile factory.

[0009] The problem of deteriorating conductivity is especially important when heavy metal free pre-treatment layers are used. Heavy metal rich pre-treatment layers tend to suffer less from this problem, which is compensated by the presence of the heavy metals. However, in all cases, it can be said that a bad surface appearance and decreased paint quality are observed as a consequence of existing curing methods.

[0010] In document CA-1196235, a near infra red furnace is used to cure the paint. The cited document describes the production line, including metal coating, pre-treatment, painting, and curing by a number of near infra red lamps, the radiation energy being adaptable to the sheet thickness, broadness, etc..., by controlling the number of lamps turned on or off.

[0011] However, the energy densities described in this document typically allow only to cure the paint layer in the way described above, meaning gradually from top to bottom, which will cause a decreased paint layer quality, especially

when heavy-metal free pre-treatment layers are applied.

Aims of the invention

5 [0012] The present invention aims to provide a method of producing pre-painted metal sheets, for example for the automobile industry, having good adhesion between the sheet and the paint layer.

Summary of the invention

10 [0013] The present invention is related to a method as defined in claim 1.
 [0014] Said method may further comprise a pre-treatment step, resulting in a pre-treatment layer on said metal substrate, said pre-treatment step being performed before said painting step. According to the invention said paint layer consists of a weldable organic paint, and said curing step is performed by high energy near infra red radiation, having an energy density of at least 400 kW/m².
 15 [0015] According to a preferred embodiment, said heating takes place in a time interval of maximum 2s.
 [0016] According to a preferred embodiment, said near infra red radiation is performed in a near infra red furnace, comprising a plurality of near infra red lamps.
 [0017] According to a preferred embodiment, said pre-treatment layer is a heavy metal free layer.
 20 [0018] The method of the invention may further comprise a metal coating step before the pre-treatment step, said metal coating step being performed in the same continuous production line as said pre-treatment step, said painting step and said curing step. Said metal coating step may be chosen from the group consisting of an electro-coating step and a hot-dip coating step.
 [0019] Said heating may be applied on one side of said substrate or on both sides of said substrate.
 [0020] In the embodiment wherein the heating is applied on both sides, said substrate may be painted on both sides.
 25 [0021] According to another embodiment, a first energy density is applied in a first part of said furnace, and a second energy density in a second part of said furnace, said first energy density being higher than said second energy density.

Short description of the drawings

30 [0022] Fig. 1 represents a schematic view of a production line according to the present invention.
 [0023] Fig. 2 is a graph showing curing times as a function of sheet thickness.

Detailed description of the invention

35 [0024] The present invention is related to a process as defined in claim 1 for producing pre-painted metal substrates, in terms of sheets, wherein the paint layer consists of a weldable paint, including the steps of painting and of curing the paint layer after painting, and preferably comprising the step of a pre-treatment of the metal sheet before said painting step. The method of the invention is particularly suited for heavy metal free pre-treatment layers. The key element of the present invention is the appropriate activation of the interface between the pre-treatment layer and a liquid organic paint layer. Before the application of the solvent or water-based weldable paint the pre-treatment layer is already dried and has formed a film or a conversion layer on the metal. Onto this layer a weldable paint layer should be linked very strongly in order to achieve good adhesion and corrosion performance but good weldability too.
 40 [0025] According to the present invention proposes the use of high energy near infra red radiation, with an energy density of at least 400 kW/m², to achieve superior activation after application of the weldable paint. The near infrared radiation should be strong enough in order to heat up the whole paint layer within a very short time, lower than 3 seconds, preferably lower than 2 seconds.
 [0026] It is the high energy radiation, which produces the advantages of the method of the invention compared to existing methods. The high energy near infra red radiation is absorbed by the whole paint layer and transferred by heat conduction into the sheet. Heat transfer at the interface polymer/metal is relatively fast, while heat transport in the metal is very fast. This means that within the short period mentioned above the paint layer and the underlying sheet will be heated to a similar temperature. The heat quickly penetrates the paint layer, which is heated up in its totality, allowing the solvents to be effectively removed before film forming of the paint layer is initiated. No cratering or forming of voids occurs during the subsequent film forming and polymerisation, so that an optimal activation of the interface between the pre-treatment layer and the soft (solvent free) paint layer is allowed to take place.
 50 [0027] Very high energy input in a short time is achieved with near infrared radiation having its energy peak at a wavelength of about 1 micron. Energy densities of 400 kW/m² and higher are necessary to allow the above-described activation. Commercially available near infrared lamps in short distance to each other using reflective refractory material together with air cooling or using highly reflective aluminium mirrors together with water-cooling allow such high energy

densities over a long period of time.

[0028] The maximum energy density (in kW/m^2) of the number of lamps can be influenced by the maximum power of each lamp (for instance 4 $\text{kW}/10$ inch) and the lamp density in width direction (for instance 1 inch between two lamps) and in coating direction (for instance 4 lamps of 10 inches long within 1 m).

5 [0029] Different pre-treatments can be applied within the scope of this invention. The pre-treatment layer is preferably thin: in the order of 0.1 to 1 μm . This layer may be obtained by an alkaline passivation of the metal layer. Preferably however, this layer is a thin organic layer, comprising epoxy, polyester or poly-urethane with the addition of complex metal ions such as Zr or Ti. Another pre-treatment layer which can be used within the scope of the present invention is a layer comprising functional molecules, such as silanes or self-assembling molecules, which are capable of forming

10 strong connections and enhance the corrosion resistance.

[0030] According to another embodiment of the present invention, the metal substrate is not subjected to a pre-treatment prior to painting. In this embodiment, the fast and high energy input, preferably by high energy near infra red radiation, makes it possible to acquire a good activation of the interface between the metal substrate's surface and the paint layer.

15 [0031] Suitable paints that can be used are for example based on Fe_3P or on Zn-particles as conductive pigments. The paints used are liquid, containing solvents such as water or organic based solvents.

[0032] According to the present invention, radiation on one side or two sides of a metal sheet is applicable. It is found that one-side curing produces a good result for sheet thicknesses up to 1.2 mm. Up to this thickness, the one sided near infra red heating allows the described global heating of the paint layer with subsequent superior paint layer quality.

20 For higher thicknesses, two-sided radiation is recommended for sheets painted on one side. The method of the present invention is especially advantageous in the case of sheets which are painted on two sides. If these sheets are subjected to a two-sided radiation, the same curing quality can be achieved in a shorter radiation time than for the same sheet painted only on one side. This effect is due to the higher heat absorption by the paint layer compared to the metal surface which exhibits a high reflectivity. This is illustrated by the laboratory results in table I, which are valid for the

25 curing of a 0.75 mm thick galvanised steel sheet, with a Zn-based paint layer applied to it. Column one is showing the radiation time in seconds and the energy output in percentage of the lamps (100% corresponding to the maximum energy density). The temperatures indicated are the paint temperatures, measured by a pyrometer, after the given time intervals.

[0033] A temperature at the end of the curing interval of ± 170 $^\circ\text{C}$ is needed to have optimal paint quality. From table 30 I it is clear that two-sided heating leads to a reduction of the curing times. Table II illustrates the effect of an additional paint layer on the other side of the metal sheet: due only to this paint layer, the temperature at the end of the same time interval, with the same radiation energy is higher. This means that sheets with two-sided coating, cured by two-sided heating, can be cured faster than one side painted sheets.

[0034] Very high energy input into a paint layer within short time is related with locally high concentrations of solvents. 35 For the interface activation to take place at high speeds, it is desirable to remove solvents and/or water rather fast. First of all the mixing of the solvents with a rather high amount of air is necessary to run at a safe level, i.e. below the lower explosion limit. Secondly, rapid removal of the gaseous solvent/water layer above the paint is necessary to allow effective penetration of the near infrared radiation into the paint layer and thus to allow a good efficiency of the near infrared radiation.

40 [0035] Due to the very fast activation of said interface and curing of the paint layer according to the present invention, an equally fast removal of solvents from the curing furnace is possible. The air speed applied over the surface to be cured, should be high enough to result in a sufficient evacuation of said solvents.

[0036] The present invention produces other advantages. The low activation and curing times allow a combination 45 of the near infrared heating section (curing of the paint) and galvanising in a single production line. Various experiments have shown that a certain temperature rise during activation is desirable in order to achieve excellent interaction between the functional groups of the heavy metal free pre-treatment and the functional groups of the paint. This temperature is independent of the sheet's thickness. This means on thinner sheet the temperature rise can be achieved by lower energy densities whilst on thicker sheet higher energy densities are recommended.

[0037] Infrared ovens are well known for their quick reaction time. A change of dimension (thickness and/or width) 50 of the sheet can be followed very quickly by an adjustment of power of the lamps and/or shut-down of sections of lamps in order to control the width of the strip.

[0038] The total number of near infra red lamps present in the furnace depends on the line speed and the curing time to be achieved. According to the preferred embodiment of the invention, the lamps used comprise a glowing wire and are installed in such a way that said wire is parallel to the transportation direction of the metal sheet through the furnace. Lamps are placed next to each other at a small distance from each other over the entire width of the furnace. The total furnace length (addition of several lamps in a row) is typically depending on the substrate's speed and the curing time.

55 [0039] According to another embodiment of the invention, the power of a first group of lamps may be put at a higher

level than a second group of lamps. For example, the first half of the lamps in the beginning of the furnace may be put at 90% of maximum output while the second half at the end may be put at 50%. This may improve the activation of said interface in certain circumstances.

[0040] Due to the very short curing time of the weldable paint, diffusion processes in the metal substrate can be suppressed. Bake-hardenable (galvanised) steel or aluminium sheets are characterised by their increase in strength due to an additional organic coating process, such as baking of a base coat during 15 to 20 min at about 170 °C, which takes place for example in the automobile factory. Pre-painted sheets as produced by the method of this invention are first deformed, assembled into a naked car body and then further covered by a sequence of coating layers: E-coat, sealer, base coat and top coat. It is an advantage of bake hardenable sheets that they show a reduced resistance to the deforming in deep drawing devices, and then gain an important portion of their mechanic properties through the bake hardening phenomenon. However, this bake hardening capability can be eliminated at the curing stage of the pre-paint process, if this curing takes too much time. The high speed of the near infrared curing process according to the invention allows to suppress diffusion processes in the sheet at higher temperatures compared with convection curing and thus retains the bake-hardenability of the sheet.

Example of a preferred embodiment

[0041] Figure 1 shows a schematic view of a production line according to a preferred embodiment of the present invention. A metal substrate 1 in the form of a continuous sheet or strip, is guided through a number of subsequent stages: the pre-treatment stage 2, the air-drying stage 3, the painting stage 4, the curing stage 5 and the cooling stage 6. In the embodiment shown, the pre-treatment is done by a first set of rollers 7, and the painting is done by a second set of rollers 8. According to the preferred embodiment, the curing furnace according to the present invention comprises near infra red lamps on each side of the substrate, each lamp producing a maximum of 4.4 kW per 10 inch.

[0042] The lamps are placed at a distance of 2 cm from each other over the width of the furnace, and installed in such a way that the heat-producing wires are parallel to the direction in which the metal substrate is transported.

[0043] The energy output of the lamps is adaptable according to the substrate's thickness and broadness, so that the energy density on one side is adaptable between 400 kW/m² and 800 kW/m². For two-sided radiation, this leads to a maximum of 1600 kW/m². The distance between the sheet and a near infra red unit is 20 mm. Typical curing times for a galvanised steel sheet with a thickness of 0.75 mm are illustrated in tables I and II.

[0044] Figure 2 shows a graph, wherein the curing time with the method according to the invention is depicted as a function of the sheet thickness, for a paint containing Zn-particles. The curve shown is valid for maximum near infra red energy density by two-sided heating (1600 kW/m²). The curve shows that this maximum density effectively allows curing within 2 seconds of sheet thicknesses up to 1.75 mm. With reduced density, for example one-sided heating at 400 kW/m², it is still possible to cure a 0.5 mm sheet within the same interval of 2s. An effective curing may also be acquired by applying more power in the beginning, and less power at the end portion of the furnace, for example 80% in the first and 20% in the second half.

Table I

(paint containing Zn-particles)				
	1-side heating		2-side heating	
	1-side painting	2-side painting	1 side painting	2-side painting
1s, 100%				194°C
1.1s, 100%			165°C	
1.8s, 100%	174°C			

Table II

(paint containing Fe ₃ P particles)				
	1-side heating		2-side heating	
	1-side painting	2-side painting	1 side painting	2-side painting
0.8s, 90%			135°C	165°C

Table II (continued)

(paint containing Fe ₃ P particles)				
	1-side heating		2-side heating	
	1-side painting	2-side painting	1 side painting	2-side painting
5	0.8s, 100%			179°C
10	1.1s, 100%		200°C	
	1.2s, 100%	177°C		

Claims

15 1. A method for producing a weldable organic paint layer on at least one side of a metal or metal coated substrate, for producing pre-painted metal sheets, said method comprising the steps of :

20 - painting a side of said substrate, resulting in a weldable organic paint layer,
- curing said paint layer by applying high energy near infra red radiation (NIR),

characterised in that during said curing step, the energy density of said Near Infra Red radiation applied on one side of said substrate is at least 400kW/m², and in that said curing takes place in a time interval less than 3 seconds.

25 2. A method according to claim 1, further comprising a pre-treatment step, resulting in a pre-treatment layer on said metal substrate, said pre-treatment step being performed before said painting step

30 3. A method according to claim 1 or 2, wherein said near infra red radiation is generated in a near infra red furnace, comprising a plurality of near infra red lamps.

4. A method according to claim 3, wherein the energy output of said lamps is variable so that the overall energy density applied on one side of the substrate can be changed between 400kW/m² and 800kW/m².

5. A method according to any of the claims 2 to 4, wherein said pre-treatment layer is a heavy metal free layer.

35 6. A method according to any one of claims 1 to 5, wherein said steps are performed in a continuous production line.

7. A method according to claim 6, wherein a metal coating step, e.g. a galvanising step, and a pre-treatment step are performed in said continuous production line, prior to said painting and curing steps.

40 8. A method according to any one of the preceding claims, said substrate is painted on one side and said heating is applied on said side which is painted.

9. A method according to any one of claims 1 to 7, wherein said substrate is painted on one side, and wherein said heating is applied on both sides.

45 10. A method according to any one of claims 1 to 7, wherein said substrate is painted on both sides of said substrate, and wherein said heating is applied on both sides.

50 11. A method according to any one of the claims 3 to 10, wherein a first energy density is applied in a first part of said furnace, and a second energy density in a second part of said furnace, said first energy density being higher than said second energy density.

55 Patentansprüche

1. Verfahren zur Herstellung einer schweißbaren, organischen Lackschicht auf mindestens einer Seite eines Metall- oder metallbeschichteten Substrats zur Herstellung von vorlackierten Metallblechen, wobei das besagte Verfahren

die folgenden Schritte umfasst:

- Lackieren einer Seite des besagten Substrats, was zu einer schweißbaren, organischen Lackschicht führt,
- 5 - Aushärten der besagten Lackschicht durch die Anwendung naher Infrarotstrahlung (NIR) unter Hochenergie,

dadurch gekennzeichnet, dass

die Energiedichte der besagten nahen Infrarotstrahlung, die während dem besagten Aushärtungsschritt auf einer Seite des besagten Substrats angewendet wird, mindestens 400 kW/m^2 beträgt, und dass das besagte Aushärten 10 in einem Zeitabstand von weniger als 3 Sekunden erfolgt.

15 2. Verfahren nach Anspruch 1, ferner umfassend einen Vorbehandlungsschritt, der zu einer Vorbehandlungsschicht auf dem besagten Metallsubstrat führt, wobei der besagte Vorbehandlungsschritt vor dem besagten Lackierungs- schritt ausgeführt wird.

20 3. Verfahren nach Anspruch 1 oder 2, wobei die besagte nahe Infrarotstrahlung in einem eine Vielzahl an nahen Infrarotlampen umfassenden nahen Infrarotofen erzeugt wird.

25 4. Verfahren nach Anspruch 3, wobei die Energieleistung der besagten Lampen varierbar ist, so dass die Gesamt- energiedichte, die auf der einen Seite des Substrats angewendet wird, zwischen 400 kW/m^2 und 800 kW/m^2 ver- ändert werden kann.

30 5. Verfahren nach irgendeinem der Ansprüche 2 bis 4, wobei die besagte Vorbehandlungsschicht eine schwerme- tallfreie Schicht ist.

35 6. Verfahren nach irgendeinem der Ansprüche 1 bis 5, wobei die besagten Schritte in einer Fließbandfertigungslinie ausgeführt werden.

30 7. Verfahren nach Anspruch 6, wobei ein Metallbeschichtungsschritt, z.B. ein Verzinkungsschritt, und ein Vorbehand- lungsschritt vor den besagten Lackierungs- und Aushärtungsschritten in der besagten Fließbandfertigungslinie aus- geführt wird.

35 8. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei das besagte Substrat auf einer Seite lackiert wird, und das besagte Erwärmen auf der besagten Seite, die lackiert ist, angewendet wird.

40 9. Verfahren nach irgendeinem der Ansprüche 1 bis 7, wobei das besagte Substrat auf einer Seite lackiert wird, und wobei das besagte Erwärmen auf beiden Seiten angewendet wird.

45 10. Verfahren nach irgendeinem der Ansprüche 1 bis 7, wobei das besagte Substrat auf beiden Seiten des besagten Substrats lackiert wird, und wobei das besagte Erwärmen auf beiden Seiten angewendet wird.

11. Verfahren nach irgendeinem der Ansprüche 3 bis 10, wobei eine erste Energiedichte in einem ersten Teil des besagten Ofens, und eine zweite Energiedichte in einem zweiten Teil des besagten Ofens angewendet wird, wobei die besagte erste Energiedichte höher liegt, als die besagte zweite Energiedichte.

Revendications

1. Procédé pour la production d'une couche de peinture organique soudable sur au moins une face d'un substrat de 50 métal ou revêtu de métal pour la production de tôles métalliques pré-peintes, ledit procédé comprenant les étapes suivantes :

- l'application d'une peinture sur une face dudit substrat pour former une couche de peinture organique soudable,
- 55 - le durcissement de ladite couche de peinture par application d'un rayonnement du proche infrarouge (NIR) de haute énergie,

caractérisé en ce qu'au cours de ladite étape de durcissement, la densité d'énergie dudit rayonnement du proche

infrarouge appliqué sur une face dudit substrat est d'au moins 400 kW/m² et **en ce que** ledit durcissement se produit dans un intervalle de temps inférieur à 3 secondes.

5 2. Procédé selon la revendication 1, comprenant en outre une étape de prétraitement pour former une couche de prétraitement sur ledit substrat de métal, ladite étape de prétraitement étant réalisée avant ladite étape d'application de peinture.

10 3. Procédé selon la revendication 1 ou 2, dans lequel ledit rayonnement du proche infrarouge est généré dans un four de proche infrarouge, comprenant une pluralité de lampes de proche infrarouge.

15 4. Procédé selon la revendication 3, dans lequel la puissance énergétique desdites lampes est variable de sorte que l'on puisse faire varier la densité d'énergie globale appliquée sur une face du substrat entre 400 kW/m² et 800 kW/m².

20 5. Procédé selon l'une quelconque des revendications 2 à 4, dans lequel ladite couche de prétraitement est une couche exempte de métaux lourds.

25 6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel lesdites étapes sont effectuées dans une chaîne de production continue.

30 7. Procédé selon la revendication 6, dans lequel une étape de revêtement de métal, par exemple une étape de galvanisation, et une étape de prétraitement sont effectuées dans ladite chaîne de production continue, avant lesdites étapes d'application de peinture et de durcissement.

35 8. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit substrat est peint sur une face et ledit chauffage est appliqué sur ladite face qui est peinte.

9. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel ledit substrat est peint sur une face et dans lequel ledit chauffage est appliqué sur les deux faces.

40 10. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel ledit substrat est peint sur les deux faces dudit substrat et dans lequel ledit chauffage est appliqué sur les deux faces.

45 11. Procédé selon l'une quelconque des revendications 3 à 10, dans lequel une première densité d'énergie est appliquée dans une première partie dudit four et une seconde densité d'énergie dans une seconde partie dudit four, ladite première densité d'énergie étant supérieure à ladite seconde densité d'énergie.

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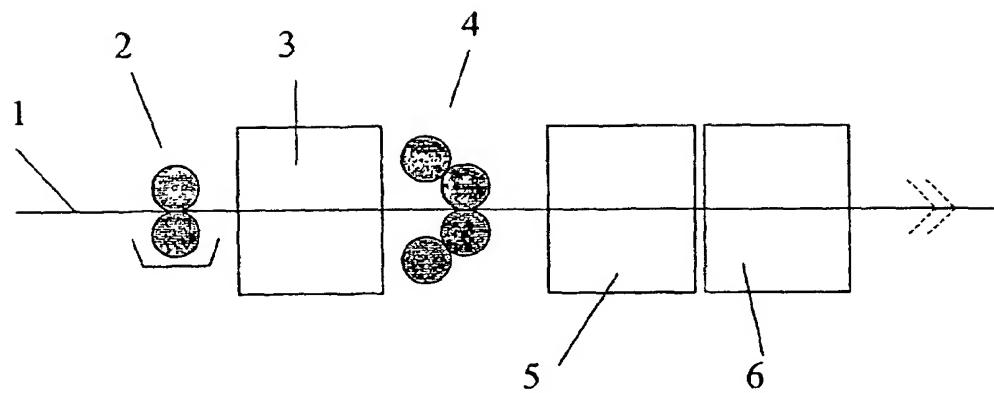


FIG. 1

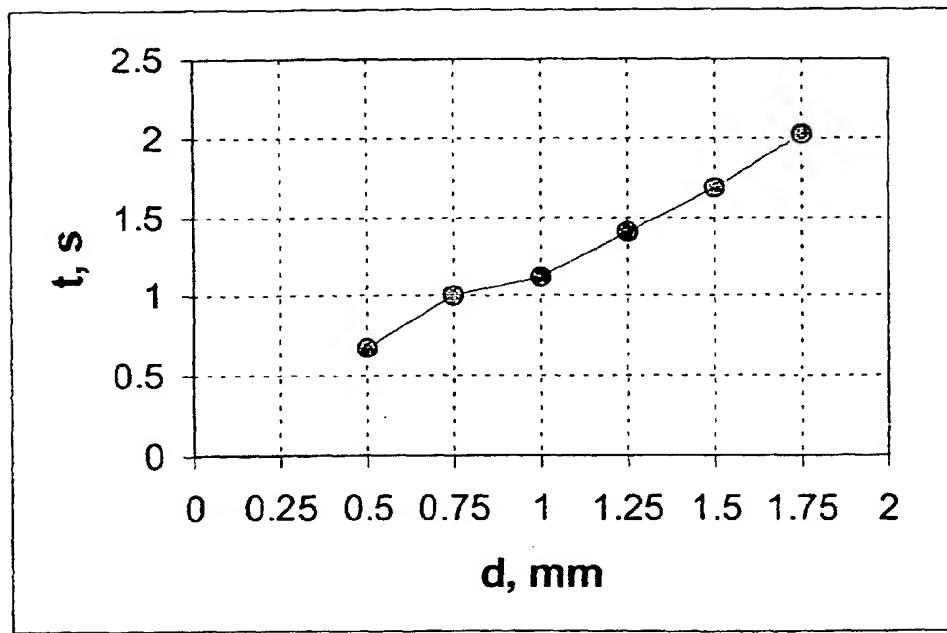


FIG. 2